

A Perspective toward Practical Lithium–Sulfur Batteries

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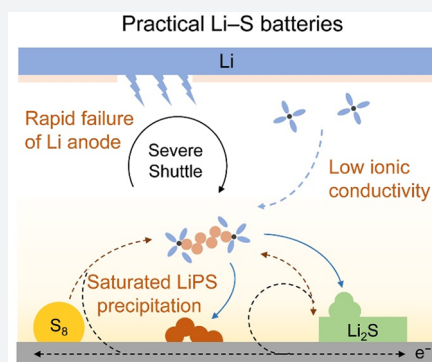


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ABSTRACT: Lithium–sulfur (Li–S) batteries have long been expected to be a promising high-energy-density secondary battery system since their first prototype in the 1960s. During the past decade, great progress has been achieved in promoting the performances of Li–S batteries by addressing the challenges at the laboratory-level model systems. With growing attention paid to the application of Li–S batteries, new challenges at practical cell scales emerge as the bottleneck. In this Outlook, the key parameters for practical Li–S batteries to achieve practical high energy density are emphasized regarding high-sulfur-loading cathodes, lean electrolytes, and limited excess anodes. Subsequently, the key scientific problems are redefined in practical Li–S batteries beyond the previous ones under ideal conditions. Finally, viable strategies are proposed to address the above challenges as future research directions.



INTRODUCTION

The pursuit of high-energy-density secondary battery systems has never been stopped. In the 1990s, lithium–ion batteries (LIBs) were successfully commercialized and rapidly occupied the worldwide energy market until today.¹ However, with the increasing demand of device duration especially under new applied situations such as unmanned aerial vehicles, the current LIB technology has gradually reached its limit.² Meanwhile, lithium–sulfur (Li–S) batteries have long been expected as a promising high-energy-density secondary battery system since their first prototype in the 1960s.^{3–5} The ultrahigh theoretical energy density up to 2600 Wh kg^{−1} and the advantages of cathode material including low cost, Earth abundance, and environmental friendliness together endow Li–S batteries as a viable scheme to realize energy density beyond 500 Wh kg^{−1}.^{6,7}

However, the development of the Li–S battery technology has never been smooth sailing.^{8,9} First, the end products of discharging and charging are intrinsically electronic/ionic insulating to render severe kinetic difficulty.¹⁰ Second, volume changes up to 80% during cycling exerts heavy pressure on the cathode integrity with rapid loss of active materials.¹¹ Furthermore, the lithium polysulfide (LiPS) intermediates dissolve in the electrolyte and shuttle between the cathode and the anode, reducing the Coulombic efficiency (CE) and cycling stability.^{12,13} Overall, the above three aspects constitute the main challenges of Li–S batteries since their first proposal.

In the past decade, numerous efforts have been devoted to overcome these above-mentioned challenges.^{14–18} In 2009, Nazar and co-workers proposed a thermal-melt treatment method to incorporate sulfur within conductive carbon matrix that significantly alleviates the insulating nature of sulfur.¹⁹ Moreover, the hierarchical porous carbon matrix helps to

mitigate the volume change and facilitate ionic conduction.^{20,21} Since then, the carbon/sulfur composite cathode has been rapidly developed with an advanced structural design and composition method to achieve progressive performances of Li–S batteries.^{22,23} To address the shuttle issue, Aurbach and co-workers studied the lithium nitrate (LiNO₃) additive that forms a protective layer on the lithium metal anode to significantly increase the CE to 98%.²⁴ Other advanced electrolyte formulas including localized high-concentration electrolyte²⁵ and ionic liquid^{26,27} are also proposed to reduce the dissolution of polysulfides. Meanwhile, cathodes that eliminate the generation of dissolved polysulfides are designed such as atomic sulfur cathode (sulfurized polyacrylonitrile)^{28–30} and small molecular sulfur (microporous carbon/S_{2–4} composites),³¹ providing an alternative path for stable Li–S batteries. In addition, constructing an interlayer also assists to confine the dissolved polysulfides within the cathode side via physical blocking, chemical adsorption, or electrostatic repulsion.^{32–34}

To particularly address the kinetic issue of the sulfur cathode, heterogeneous polysulfide electrocatalysis and homogeneous polysulfide redox mediations have been recently developed.^{35–37} Polysulfide electrocatalysis aims to accelerate the cathode redox kinetics by reducing the activation energy barriers.³⁸ Various polysulfide electrocatalysts including

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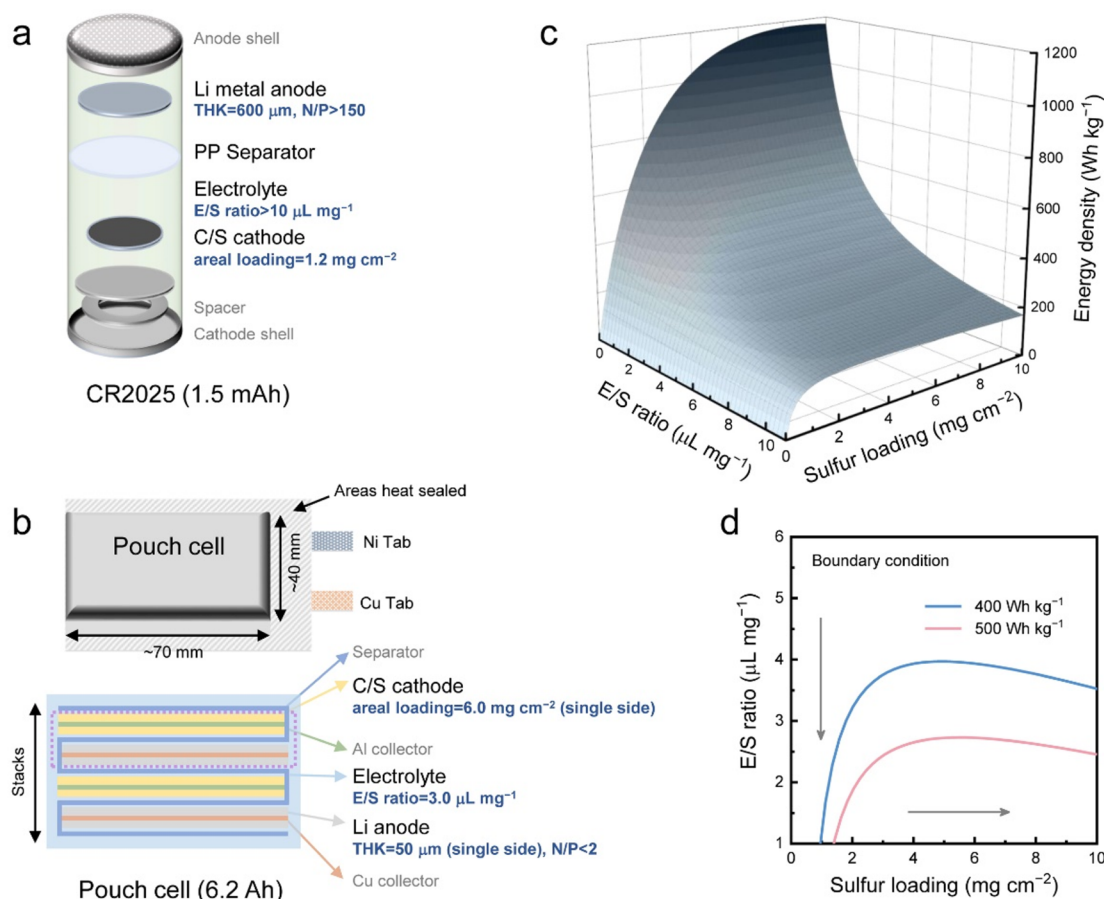


Figure 1. Estimation of the actual energy density of Li–S batteries. Schematic illustration of (a) a Li–S coin cell and (b) a Li–S pouch cell. (c) Calculated gravimetric energy densities of a Li–S pouch cell depending on areal sulfur loading and E/S ratio. (d) Boundary condition of a Li–S pouch cell with a targeted specific energy of 400 and 500 Wh kg^{−1}.

metals,³⁹ metal compounds,^{40,41} heteroatom-doped carbon,⁴² and other organic composites^{43,44} demonstrate performance advantages in reducing polarization, improving the rate response, and extending the cycling lifespan. On the other hand, polysulfide redox mediation regulates a targeted sulfur redox reaction by introducing an extrinsic kinetically favorable redox couple that participates in the intrinsic sulfur redox reaction.⁴⁵ Typical redox mediators can increase the deposition dimension and specific capacity of lithium sulfide (Li₂S),⁴⁶ reduce the Li₂S oxidation overpotential during charge,⁴⁷ or promote the reduction of S₈ depending on the electrochemical potential of the redox mediators.⁴⁸ All of the above efforts have contributed to greatly enhanced Li–S performances, including an ultrastable cycle of over 1500 cycles,^{49,50} a high specific capacity of over 1500 mAh g^{−1},^{51,52} or an excellent rate performance of more than 40 C.^{53,54}

However, it is worth noticing that most of the performance promotion is realized at the laboratory level under ideal conditions such as low sulfur loading around 1.0 mg_S cm^{−2}, high electrolyte volume with the electrolyte to sulfur ratio (E/S ratio) over 10 μL mg_S^{−1}, and excessive lithium anode with the negative to positive electrode ratio (N/P ratio) over 150 (Figure 1a).^{55–59} Although the above conditions are conducive to the improvement of specific capacity and cycling stability under coin cell evaluation, high-energy-density Li–S batteries are utterly impossible to be realized under such conditions. Moreover, the performance improvements may mislead the research direction to ignore the huge gap between laboratory

coin cells and practical pouch cells under working conditions. Bearing in mind the original and intrinsic advantage of Li–S batteries being high energy density, electrochemical evaluation in pouch cells with high-sulfur-loading cathodes, low E/S ratio, and ultrathin lithium metal anode is important to provide solid guidance for practical Li–S batteries (Figure 1b).

To achieve a target energy density of 400 or 500 Wh kg^{−1}, herein we evaluate the key parameters of a practical Li–S pouch cell using a routine carbon/sulfur composite cathode and ether electrolyte as a model. The mass of the involved components is based on previous reports.⁵⁵ Among them, the mass of separators, current collectors, and packing is fixed, while the remaining components including binder, lithium anode, conductive carbon, and electrolyte change with the sulfur loading. It is assumed that the carbon/sulfur composite contains 83 wt % sulfur and further mixed with a binder in a weight ratio of 9:1, and the N/P ratio is fixed to be 2.0. In addition, an increase in areal sulfur loading will inevitably impair the actual discharge specific capacity. Therefore, each additional 1.0 mg cm^{−2} sulfur loading is assumed to result in a specific capacity reduction of 30 mAh g^{−1} and a voltage drop of 10 mV. On the basis of the above assumptions, the actual energy density of the Li–S pouch cell is estimated using the following equation.

$$E_g = \frac{E \times Q \times M_s}{M_{\text{total}}}$$

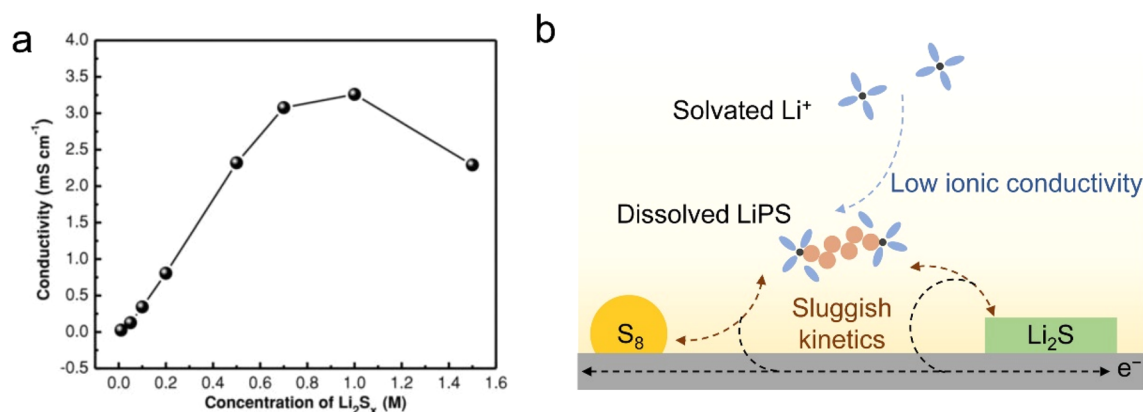


Figure 2. Low ionic conductivity of practical Li–S batteries. (a) The relationship between the ionic conductivity and the polysulfide concentration in DME solvent.⁶⁰ (b) Schematic illustration of sulfur redox reactions with high LiPS concentration. The LiPS kinetics on electrode surface deteriorates due to the slow lithium ion transportation.

where E is the average discharge voltage, Q is the specific discharge capacity based on sulfur, M_s is the areal sulfur loading, and M_{total} is the total weight of the Li–S pouch cell.

The relationship between the estimated actual energy density of the Li–S pouch cell with areal sulfur loading and E/S ratio is established (Figure 1c). As the sulfur loading increases, the energy density first increases sharply and then decreases gradually, implying an optimal range of sulfur loading in cell design. On the other hand, the energy density increases significantly as the E/S ratio decreases for a fixed sulfur loading, especially for the cells with high sulfur loading. Nevertheless, the E/S ratio cannot be reduced infinitely considering the specific capacity of sulfur and the cycling lifespan to be met. On the basis of the above simulations, the optimal parameters for a 400 Wh kg^{−1} Li–S pouch cell include an areal sulfur loading of 5.0 mg_s cm^{−2} and an E/S ratio of 4.0 μL mg_s^{−1} (Figure 1d). When the energy density target increases to 500 Wh kg^{−1}, the two parameters are supposed to be 6.0 mg_s cm^{−2} and 2.5 μL mg_s^{−1}, respectively. Besides, the excess of metal lithium anode under practical conditions must be strictly controlled due to the economic costs. Therefore, practical high-energy-density Li–S batteries can be achieved with an areal sulfur loading higher than 5.0 mg_s cm^{−2}, an E/S ratio lower than 4.0 μL mg_s^{−1}, and a N/P ratio less than 2.0. These restrictions are of vital importance for further development of practical Li–S batteries in terms of high energy density.

Considering the key parameters of areal sulfur loading, E/S ratio, and N/P ratio are very different between ideal and practical conditions, it is rational to understand the huge gap between Li–S coin cells and pouch cells that the excellent Li–S performances in coin cells can hardly be reproduced in pouch cells by simple amplification. Besides, changes such as the tap introduction, internal pressure, and electrolyte flowability also lead to spatially uneven electrochemical reactions in pouch cells and premature failure of the overall battery performance. On one hand, pouch cell-level evaluation is therefore emphasized for the development of practical Li–S batteries. On the other hand, coin-cell level evaluation is also important to afford comprehensive information as a guidance for fundamental understanding of basic Li–S chemistry and design strategies of practical Li–S batteries.

■ CHALLENGES REDEFINED IN PRACTICAL LITHIUM–SULFUR BATTERIES

The proposed restrictions to achieve actual high energy density define the boundaries of practical Li–S batteries. With the traditional challenges of insulating active materials, volume change, and polysulfide shuttle being addressed, new challenges emerge in practical Li–S batteries and become the bottleneck to realize actual high energy density. Therefore, these emerging challenges shall be redefined in the first place to guide further research in understanding the Li–S chemistry different from that under ideal conditions and developing regulation strategies for the development of practical Li–S batteries, which are discussed as follows:

- (1) **Low ionic conductivity.** For a commonly used ether-based electrolyte of 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (v/v = 1/1) with 1.0 mol L^{−1} lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 2 wt % LiNO₃, the ionic conductivity is sufficient for initial electrochemical reactions to take place. However, the sulfur redox reactions go through a dissolution–precipitation pathway that massive LiPSs dissolve in the electrolyte. Especially with high-sulfur-loading cathodes and under lean electrolyte conditions, the polysulfide concentration can be as high as 7 mol_[S] L^{−1}. With such a high LiPS concentration, the viscosity increases to significantly reduce the electrolyte ionic conductivity according to the Stokes–Einstein relationship (Figure 2a).⁶⁰ In addition, the dissolved LiPSs interact with free solvents through solvation and even with lithium salts by forming clusters to reduce ionic conductivity.⁶¹ Consequently, low ionic conductivity caused by concentrated LiPS affords additional kinetic obstructs on the sulfur redox reactions manifested by large polarization of the second discharge plateau and poor rate performances compared with ideal conditions (Figure 2b). Enlarged ohmic polarization can therefore be a possible reason for battery failure especially in practical Li–S pouch cells, which shall be taken seriously as an emerging main challenge.
- (2) **Saturated and premature precipitated LiPSs.** Generally, LiPSs from long-chain Li₂S₈ to short-chain Li₂S₄ are supposed to be soluble in ether-based electrolyte, although the solubility of Li₂S₄ is relatively lower.⁶² Such an argument is valid when the E/S ratio is high

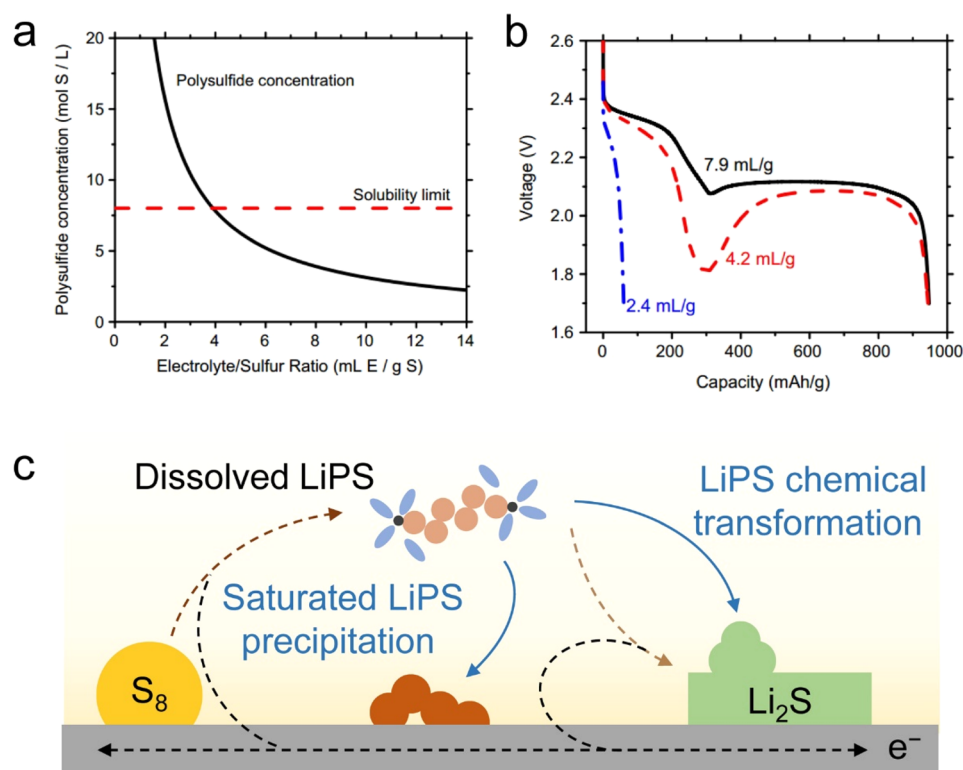


Figure 3. Saturated and prematurely precipitated LiPSs in practical Li–S batteries. (a) Polysulfide concentration in correlation with the E/S ratio supposing all sulfur is dissolved. (b) Galvanostatic discharge curves for Li–S cells at three different E/S ratios.⁶³ (c) Schematic illustration of spatially uneven electrochemical reactions on the cathode surface in Li–S batteries with lean electrolyte.

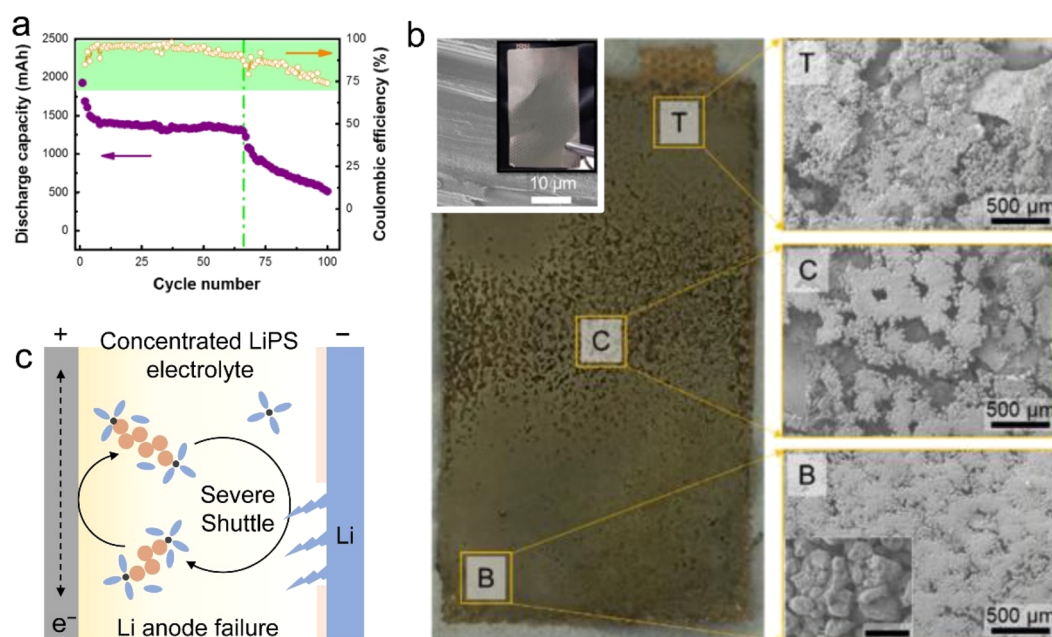


Figure 4. Rapid lithium metal anode failure in practical Li–S batteries. (a) Cycling performance of a Li–S pouch cell.⁶⁵ (b) Optical images of lithium metal anode with corresponding scanning electron microscopy images before (inset) and after 40 cycles at different regions including the bottom (B), top (T), and central (C) regions.⁶⁶ (c) Schematic illustration of lithium corrosion due to severe concentrated LiPS shuttle in practical Li–S batteries.

under ideal conditions in coin cells. However, with the E/S ratio as low as $3.0 \mu\text{L mg}^{-1}$ in practical Li–S pouch cells, high LiPS concentration can be over $10 \text{ mol}_{[\text{S}]} \text{ L}^{-1}$ and consequently exceed the dissolution limit and result in saturation and premature precipitation of LiPSs

(Figure 3a).⁶³ The premature precipitation of LiPSs on conductive matrix blocks the electronic/ionic conduction pathway and forces kinetically sluggish solid–solid conversion to take place. Previous research studies have verified the above argument that the

polarization of the second discharge plateau referring solid precipitation becomes large enough at relative low E/S ratios to reach the voltage cutoff and significantly reduce specific capacity (Figure 3b).⁶⁴ Therefore, the saturation and premature precipitation of LiPSs exert great pressure on the electrochemical kinetics of sulfur conversion in practical Li–S pouch cells that induce a dramatically rapid battery failure. In addition, the chemical comproportionation and disproportionation of polysulfides become more dominant with higher LiPS concentration, affording increased deposition dimensions and large solid aggregates that tend to lose electrical contact during cycling. Consequently, the Li–S chemistry is very different from that under ideal conditions with distinct electrochemical processes and a new balance between the electrochemical pathway and the chemical pathway. The emerging challenge of LiPS saturation and premature precipitation requires new insights regarding the fundamental understanding and effective regulation strategies as the second.

- (3) Rapid failure of lithium metal anode. Electrochemical evaluation in Li–S coin cells usually employs thick lithium metal anodes with the N/P ratio higher than 150. Under such ideal conditions, the failure of the lithium metal anode is covered, performing as a gradual specific capacity decrease within several hundreds of cycles. However, Li–S pouch cells usually go through a rapid failure with dramatic capacity loss in only several cycles (Figure 4a). The cycled lithium anode displays a highly uneven morphology where several regions are severely corroded in a failed pouch cell (Figure 4b), and further analyses identify anode failure as the main reason. The cause of battery failure from gradual cathode capacity loss in coin cells to rapid capacity decrease in pouch cells mainly results from the following three aspects: (i) Higher actual current density and cycling

capacity applied on the Li metal anode using high-sulfur-loading cathodes that aggravate uneven lithium deposition and anode volume change;⁶⁵ (ii) higher LiPS concentration and a more severe shuttle effect that render serious lithium corrosion by LiPSs;⁶⁶ (iii) low N/P ratio with less lithium excess which cannot support the continuous irreversible loss of active lithium by reacting with LiPS or electrolyte (Figure 4c). Thereby, the failure of lithium metal anode becomes the main reason for practical Li–S pouch cells. In addition, the growth of dendrites, pulverization, and gas-generated reactions at

New challenges are redefined under these boundaries regarding low ionic conductivity of high-concentrated LiPS electrolyte, saturation and premature precipitation of LiPSs, and rapid failure of lithium metal anode.

the surface of lithium anode also pose a threat to battery safety, which shall be seriously considered under working conditions. When addressing the above issue, the existence of massive LiPSs in the electrolyte is essential as the precondition to evaluate the protection strategies of lithium metal anodes in Li–S pouch cells, together with other rigorous conditions including high cathode capacity and low N/P ratio. The lithium metal chemistry under such rigorous conditions needs more attention.

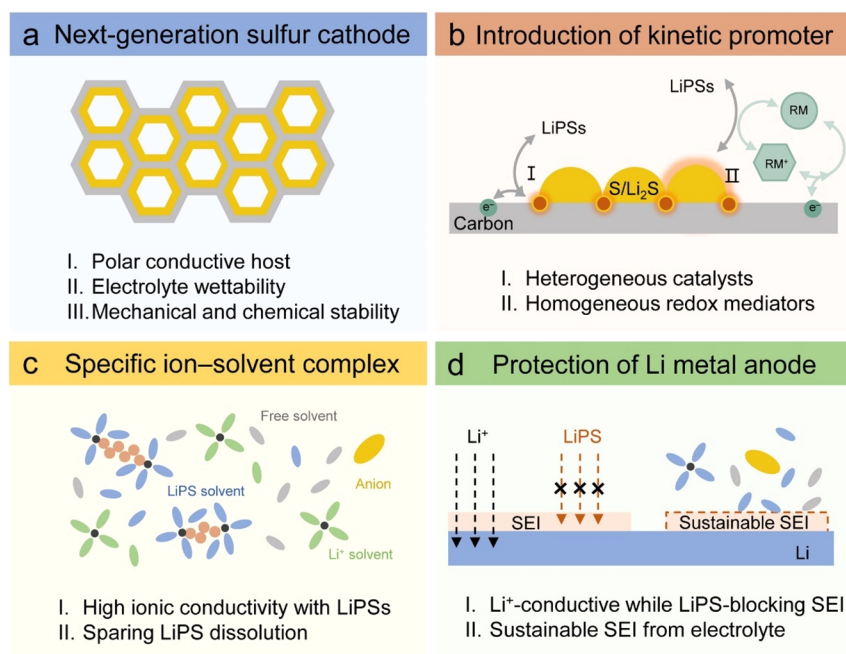


Figure 5. Guidelines of advanced practical Li–S batteries. (a) Design of next-generation sulfur cathode. (b) Introduction of kinetic promoters. (c) Design of specific ion–solvent complex in the electrolyte. (d) Protection of the lithium metal anode.

■ GUIDELINES OF PRACTICAL LITHIUM–SULFUR BATTERIES

In order to ensure the intrinsic advantage of Li–S batteries being high energy density, the application of practical Li–S batteries must employ a high-sulfur-loading cathode, lean electrolyte, and limit anode excess. New challenges are redefined under these boundaries regarding low ionic conductivity of high-concentrated LiPS electrolyte, saturation and premature precipitation of LiPSs, and rapid failure of lithium metal anode. These new challenges indicate distinct Li–S chemistry from that under ideal conditions with different key processes and failure mechanisms. To address these emerging challenges in practical Li–S batteries, the following four directions require extensive efforts and are expected with essential advances in future.

(1) Next-Generation Sulfur Cathode. The design of carbon/sulfur composite cathode has been proven to be a great success to propel the development of secondary Li–S batteries with potential high energy density.^{67–69} In consideration of the restriction of high sulfur loading and lean electrolyte, the conductive carbon matrix is expected with further functions to address the new challenges beyond the existing requirements (Figure 5a). Polar carbon hosts (either heteroatom-doped carbon or hybrids with transition metal compounds) demonstrate favorable interactions with LiPSs in many reports,³⁷ and therefore polarity besides conductivity shall be recognized as an additional necessary factor for the design of the carbon matrix. Second, electrolyte wettability needs to be taken seriously under lean electrolyte conditions. Improved electrolyte wettability guarantees sufficient ionic conduction pathways and high utilization of the cathode sulfur, while it leaves more electrolyte for ion conduction and anode consumption during cycling. To this end, the structure of the composite cathode regarding carbon porosity, sulfur distribution, and binder selection requires careful reconsideration. Third, mechanical and chemical stabilities of the carbon matrix are again emphasized under high-sulfur-loading conditions that a dramatic phase change takes place continuously within the cathode. A robust conductive scaffold is a prerequisite. Besides, material cost and manufacturability should also be considered.

Despite the previous reports of high-performance sulfur cathodes under ideal conditions, rational design principles of the cathode remain controversial especially for high-sulfur-loading cathodes with lean electrolyte. Instead of more trial-and-error efforts, insights are needed to understand the evolution of practical sulfur cathodes under working conditions. Information such as sulfur spatial distribution and electrolyte penetration can be very helpful, where *in situ* or *operando* observations are very helpful yet require more attentions to develop applicable methods. Overall, the success of the carbon/sulfur composite cathode has come to a consensus, and the next-generation sulfur cathode for practical Li–S batteries is on its way.

(2) Introduction of Kinetic Promoter. Poor redox kinetics has always been an intrinsic difficulty for the sulfur redox reactions that take place at multiphase boundaries along with severe phase migration. Various kinetic promoters such as oxide,¹¹ sulfide,⁷⁰ nitride,^{71,72} polymer,⁷³ and framework materials⁷⁴ have demonstrated performance advantages in many aspects from rate performance to long lifespan.^{75,76} Kinetic promoters can be generally divided into heterogeneous

electrocatalysts and homogeneous redox mediators as discussed above, both of which have been investigated regarding the mechanism and the performance.

For a practical Li–S pouch cell with high-concentrated LiPS electrolyte and premature precipitated LiPSs, kinetic promotion is particularly essential to facilitate the sulfur redox reactions (Figure 5b). However, simple introduction of the reported kinetic promoters may not definitely result in performance promotion considering the huge gap between coin cells and pouch cells. For a polysulfide electrocatalyst, its mass ratio shall be limited not to influence the overall energy density, and therefore how to make the most utilization of polysulfide electrocatalysis requires careful considerations. In addition to the selection of high-performance electrocatalysts, their configuration also matters. Constructing an electrocatalytic interlayer between the cathode and the separator affords a promising scheme, where more investigation is required. For a redox mediator, its own shuttle can reduce the CE and even corrode the lithium metal anode.⁷⁷ Fixation of homogeneous redox mediators within the cathode side can address the above side effect; yet, the full reservation of the redox mediation capability requires delicate design. Meanwhile, a redox mediator generally regulates a target process with a narrow voltage range. Therefore, multirange redox mediators are potentially needed but will improve the complexity of practical Li–S batteries. Nevertheless, kinetic promoters have proven themselves to be highly effective in facilitating the sulfur redox reactions, and the introduction of kinetic promoters is an emerging direction for overcoming the challenges in practical Li–S batteries.

(3) Design of Specific Ion–Solvent Complex in Electrolyte. The development of electrolyte drives the revolution of Li–S batteries from LiPS-dissolved tetrahydrofuran and dimethyl sulfoxide to LiPS-insoluble ionic liquid and fluorinated ether, where the currently employed DOL/DME ether-based electrolyte affords a moderate LiPS solubility.^{78–80} Each electrolyte formula defines a unique Li–S conversion pathway and diversifies the Li–S chemistry. The current widely employed ether-based electrolyte supports the dissolution–precipitation pathway with a certain degree of dissolved LiPS for smooth sulfur redox.⁸¹ Unfortunately, more and more evidence indicates the current ether-based electrolyte is incapable to endow long-cycling Li–S batteries under practical conditions.^{82,83} To address the new challenges in practical Li–S batteries, innovation of the Li–S electrolyte is of great significance, and the following discussion can help to provide a general guideline for future research (Figure 5c).

(i) High ionic conductivity with high-concentrated LiPSs. The concentration of LiPSs in the electrolyte is always changing during discharge/charge, and high-concentrated LiPSs have a great influence on the overall properties of the electrolyte under a low E/S ratio. Therefore, besides the evaluation of the original electrolyte without LiPSs, high-concentrated LiPS electrolytes especially LiPS saturated solutions need more attention. Physicochemical properties, electrochemical reactive features, and compatibility with the cathode and the anode need to be clarified. High ionic conductivity should be realized with the existence of LiPSs.

(ii) Sparing LiPS dissolution. For a carbon/sulfur composite cathode undergoing the dissolution–precipitation pathway, dissolved LiPS is essential to bridge the solid end products. However, under lean electrolyte conditions and with limited lithium excess, concentrated LiPSs result in cathode kinetic

sluggishness, low electrolyte ionic conductivity, and anode corrosion as discussed above. To this end, a sparing LiPS dissolution electrolyte may settle the dilemma with the dissolved LiPSs sufficient to render smooth sulfur conversion and not to significantly influence the electrolyte and anode. The sparing LiPS dissolution electrolyte herein refers to a relative low LiPS concentration compared with that in common ether-based electrolytes rather than complete insolubility of the LiPSs that the dissolution–precipitation pathway is expected to be maintained. Nevertheless, it requires further comprehensive investigations to define an optimal LiPS concentration range and corresponding electrolyte formula. The sparingly LiPS dissolved electrolyte shall balance the requirements from both the cathode and the anode.

To realize high ionic conductivity and sparing LiPS dissolution, a single-component and single-function solvent that renders a similar ion–solvent complex for lithium ions and LiPSs is less competitive. Designing specific ion–solvent complexes for lithium ions and LiPSs is more rational for them to contribute distinct functions separately. The ion–solvent complex for lithium ions needs to provide sufficient ionic conductivity and reversible lithium stripping/plating, while the ion–solvent complex for LiPSs is expected to protect the LiPSs from interacting with lithium ions or lithium metal and support the cathode redox reactions at the same time. Therefore, at least two solvents targeting lithium ions and LiPSs are needed. Also, a diluent is possibly needed to reduce the viscosity caused by concentrated LiPSs as a third component. It is worth noticing that anions can participate in the ion–solvent complex, and their influence also requires research attention. In addition, the sparing LiPS dissolution electrolyte design may reduce the sulfur redox kinetics to some extent. Therefore, the employment of a next-generation sulfur cathode and the introduction of kinetic promoters are of greater significance in Li–S pouch cells with the sparing LiPS dissolution electrolyte.

(4) Protection of Lithium Metal Anode. Strategies of lithium metal anode protection have been massively reported in lithium metal batteries.^{84–92} However, the existence of concentrated LiPSs renders additional problems of continuous LiPS shuttle and anode corrosion. The solid electrolyte interface (SEI) formed on the lithium metal surface plays a decisive role in determining the lithium stripping/plating behaviors,^{93–95} and the SEI in Li–S batteries is expected with an additional function to selectively block LiPSs from interacting with the lithium metal anode beyond the protective functions in lithium metal batteries (Figure 5d). However, the generation of such an advanced SEI is highly challenging. Electrolyte regulation, artificial coating, and pretreatment are potential feasible methods.

Furthermore, the as-generated SEI cannot be considered to be absolutely stable because the surface of lithium metal varies significantly during cycling. Therefore, in spite of the original well-designed protective SEI, the newly deposited lithium metal reacts with the electrolyte to form subsequent SEI, and the subsequent SEI can even dominate the lithium stripping/plating behaviors as the main component within prolonged cycles.⁹⁶ Hence, sustainable SEI is highly considered besides the originally designed SEI to afford a continuous protective layer on Li metal. The combination of artificial SEI and electrolyte-derived sustainable SEI is expected to synergistically extend the lifespan of the lithium anode. The role of concentrated LiPSs on forming the subsequent SEI shall also

be taken seriously, which is supposed to contribute to the subsequent SEI distinct from that in lithium metal batteries. Besides, the design of sustainable SEI should avoid harmful side reactions such as gas production and other hazards to pouch cells. On the basis of the premise of a favorable SEI that fulfills the above requirements, the introduction of a lithium host to construct a composite lithium metal anode can further effectively extend the lifespan of practical batteries, benefiting from relieved volume change, reduced local current density, and controllable lithium affinity modification to reduce the nucleation barrier. Otherwise, without the desired SEI, the introduction of the lithium host may result in more severe consumption of the electrolyte and side reactions with LiPSs.

New opportunities exist with distinctive phenomena and mechanisms to be revealed while exploring exciting Li–S chemistry under practical conditions.

CONCLUSION

Remarkable advances have been made on developing high-performance Li–S batteries in the past decade with in-depth understanding of fundamental Li–S chemistry and regulation strategies from electrode design to electrolyte modulation. To fulfill the original goal and realize the intrinsic advantage of actual high energy density, more attention should be paid to practical Li–S batteries with high-sulfur-loading cathodes, lean electrolyte, and limited anode excess. Such restrictions redefine the research boundaries, and new challenges emerge as the bottleneck of practical Li–S batteries regarding low ionic conductivity to render large ohmic polarization, saturation and premature precipitation of LiPSs to cause kinetic difficulty, and rapid lithium metal anode failure in Li–S pouch cells. On one hand, these new challenges raise higher requests for targeted and sufficient regulation strategies under complex practical conditions. On the other hand, new opportunities exist with distinctive phenomenon and mechanisms to be revealed while exploring exciting Li–S chemistry under practical conditions. Furthermore, in-depth investigations on the novel Li–S chemistry will afford fresh insights and enlighten other essential energy-related processes based on multielectron and multiphase electrochemical reactions.

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Notes

The authors declare no competing financial interest.

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